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Tributylphosphine catalyzed addition of diphenylphosphine oxide to unsubstituted and substituted electron-deficient alkenes

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ABSTRACT

The PBu_3-catalyzed conjugate addition of diphenylphosphine oxide to unsubstituted and substituted electron-deficient alkenes is reported. β-Substituted α,β-unsaturated esters, *trans*-methyl crotonate and *trans*-methyl cinnamate, known for their reluctance to participate in phosphine-catalyzed transformations, also react well under the developed conditions. Mild reaction conditions, simple work-up and the ease of catalyst recovery make the proposed methodology useful for the preparation of functionalized tertiary phosphine oxides. The utility of this method was demonstrated by the gram-scale reactions of diphenylphosphine oxide with electron-deficient alkenes.

Introduction

Tertiary phosphine oxides represent an important class of organophosphorus compounds with applications in industrial chemistry and the life sciences. The reduction of tertiary phosphine oxides provides convenient access to tertiary phosphines, which are broadly applied in organometallic catalysis and organocatalysis.[1] Due to their hydrolytic, thermal and oxidative stability, tertiary phosphine oxides are versatile ligands for the extraction of transuranic,[2] rare-earth[3] and noble metals;[4] as well as the stabilization of quantum dots and other metal nanoparticles.[5] Furthermore, tertiary phosphine oxides are well-established flame retardants for polymers.[6] Consequently, the development of novel efficient methods for the preparation of tertiary phosphine oxides is highly appealing.

One of the most atom-economical and straightforward approaches for the synthesis of tertiary phosphine oxides is the addition of secondary phosphine oxides to unsaturated species, known as the Pudovik reaction or phospha-Michael addition.[7] Due to the relatively low reactivity of the P(O)–H bond, the direct addition to activated carbon-carbon multiple bonds typically occurs only at high temperature.[8] In order to proceed under milder conditions, the reaction can be catalyzed by organic and inorganic bases such as alkaline alkoxides (e.g. MeONa, EtONa), KOH, $Ca(OH)_2$, NaH, *n*-BuLi, Et_2Zn;[7,9] transition metal salts;[10] or radical initiators such as AIBN.[11] Despite the abundance of examples where tertiary phosphines are used as organocatalysts in Michael-type additions for carbon-carbon and carbon-heteroatom bond formation,[12] there exist only a few reports regarding the phosphine-catalyzed Pudovik reaction. Recently, Han and co-workers introduced PMe_3 as an efficient and easily removed catalyst for the addition of dialkyl phosphites, alkyl *H*-phosphinates and secondary phosphine oxides to electron-deficient alkenes.[13] Our group, as well as Kim and co-workers, developed an efficient PBu_3-catalyzed Pudovik reaction, that can be performed without a protective inert atmosphere and easy catalyst recovery.[14] The scope of this reaction was examined with several electron-deficient alkenes, and it was noted that best yields and shortest reaction times were achieved when the concentration of PBu_3 was varied with respect to the nature of unsaturated reagent (typically, 5–50 mol% of the catalyst were required).[14b,c]

However, secondary phosphine oxides have not been tested for the PBu_3-catalyzed P(O)–H bond addition reaction, which stimulated us to explore the scope of this reaction using diphenylphosphine oxide as a substrate.

Results and discussion

Initially, the model reaction of diphenylphosphine oxide with methyl methacrylate in the presence of PBu_3 was examined under the conditions developed previously for the reaction using dialkyl

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